

An environmentally friendly microextraction method for the determination of cadmium in water samples

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Abstract

Switchable solvents have shown promise as alternative solvents for extraction processes due to their ability to be switched between polar and nonpolar states, which allows for selective extraction of target compounds from complex matrices. A switchable solvent-based microextraction method was developed for the environmentally friendly determination of cadmium ions using flame atomic absorption spectrometry (FAAS). The method utilized N,N-dimethyl-n-octylamin (DMOA) and 1-(2-Pyridylazo)-2-naphthol (PAN) as switchable solvent and ligands, respectively. Important parameters such as pH, amount of extraction solvent and ligand, sample volume, and the effects of NaOH and foreign ions were optimized. The limits of detection and quantification and preconcentration factor were determined to be 0.63 $\mu\text{g L}^{-1}$, 2.1 $\mu\text{g L}^{-1}$, and 60, respectively. The validation study of the method involved spiking a fixed amount of cadmium to the water samples and determining the recovery. The method was successfully applied to determine the cadmium ion content in various environmental water samples.

Keywords: Cadmium, microextraction, environmental friendly method

Su örneklerindeki kadmiyumun belirlenmesi için çevre dostu bir mikroekstraksiyon yöntemi

Öz

Polaritesi değiştirilebilir çözücüler, polar ve nonpolar durumları arasında geçiş yapabilme özellikleri nedeniyle, karmaşık matrislerden hedef bileşiklerin seçici olarak ekstraksiyonu için alternatif çözücüler olarak umut vaat etmektedir. Yeni bir çevre dostu değiştirilebilir çözücü temelli mikroekstraksiyon yöntemi, alevli atomik absorpsiyon spektrometresi kullanarak kadmiyum iyonlarının tayini için geliştirilmiştir. Yöntemde değiştirilebilir polariteli çözücü olarak N,N-dimetil-n-oktilamin ve ligand olarak 1-(2-Piridilazo)-2-naftol kullanılmıştır. pH, ekstraksiyon çözücüsü ve ligand miktarı, örnek hacmi, NaOH ve yabancı iyonların etkileri gibi önemli parametreler optimize edilmiştir. LOD, LOQ ve ön zenginleştirme faktörü sırasıyla 0.63 mg L^{-1} , 2.1 mg L^{-1} ve 60 olarak belirlenmiştir. Yöntemin doğrulama çalışması, belirli bir miktarda kadmiyumun su örneklerine ilave edilmesi ve geri kazanımın tayini ile gerçekleştirilmiştir. Yöntem, çeşitli çevresel su örneklerinde kadmiyum iyon içeriğinin tayini için başarılı bir şekilde uygulanmıştır.

Anahtar Kelimeler: Kadmiyum, mikroekstraksiyon, çevre dostu metod.

1. Introduction

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In the early 1900s, as industrialization rapidly spread, environmental pollution problems began to surface. Heavy metals have been identified as a significant cause of environmental pollution. Among the heavy metals, cadmium is considered one of the most hazardous pollutants in the ecosystem, as it is toxic to living organisms and can have adverse effects on the kidney, lung, stomach, and intestinal system. Various sources contribute to the presence of cadmium in the environment, including paints, batteries, cigarette smoke, plastic additives. When these sources are discarded or released into the environment, cadmium is released and can mix with water. Leakage from these sources can contaminate water sources and soil, leading to cadmium entering the human body through the food chain and drinking water. Therefore, water sources are considered one of the most important routes of cadmium exposure to humans [1-2].

Various instrumental methods like AAS, ICP-AES, and ICP-MS can be utilized to determine the amount of cadmium in water resources with high accuracy and sensitivity. In addition, separation /preconcentration methods are widely used in trace level cadmium analyses as in water resources. In order to prevent from matrix effect and to bring the analyte concentration above the detection limit of the instruments [3-8].

Solid phase extraction (SPE), cloud point extraction (CPE), coprecipitation, liquid-liquid extraction is among the most used separation /preconcentration methods [9-11]. In recent years, these methods have been replaced by methods that support the principles of green chemistry in micro quantities. These methods can be classified into two main categories: solid phase microextraction (SPME) and liquid phase microextraction (LPME). Dispersive liquid-liquid microextraction (DLLME), Solidifiedfloating organic drop microextraction (SFODME), switchable solvent based microextraction (SS-LPME) can be given as examples for the liquid phase microextraction method [12-14]. These methods are environmentally friendly, low-cost, high-yield, time-saving, low-risk, reliable, and friendly to living and non-living environments with simpler steps and less harmful or harmless substances.

Nonpolar secondary and tertiary amines can be used to create switchable hydrophilicity solvents. By introducing CO₂, the solvents become hydrophilic, but the addition of NaOH removes the CO₂ and restores their hydrophobic properties. These solvents are utilized in the switchable solvent-based microextraction technique and offer significant benefits such as affordability, environmental safety, ease of accessibility, and have been widely used for heavy metal detection in water samples in recent times. [15-20].

Overall, the study presents an effective and environmentally friendly microextraction method for the determination of Cd(II) ions in water samples. The use of switchable solvents in this method offers several advantages over traditional solvent extraction techniques, and the practicality and ease of use make it a valuable tool for routine water analysis.

2. Material and Methods

2.1 Reagent and Apparatus

Analytical reagent grade reagents were used throughout the study. N, N-dimethyl-n-octylamine (DMOA) and 1-(2-Pyridylazo)-2-naphthol (PAN) were obtained from Sigma Aldrich. NaOH, 65 % HNO₃ and Cd(NO₃)₂ were purchased from Merck.

The pH was adjusted with phosphate buffer solution and measured with a Mettler Toledo pH meter. Cd (II) ions analyses in aqueous samples were done with Analytik jena Zeenit 700 Flame Atomic Absorption Spectrophotometer.

2.2 Preparation of Extraction Solution

The general procedure of synthesis of protonated N, N-dimethyl-n-octylamine (P-DMOA) was described in a previous work [3,21].

2.3 Experimental procedure

To prepare the sample, a 10 mL solution containing 0.5 mg L^{-1} Cd was placed in a 25 mL tube and the pH was adjusted to 8.5 using phosphate buffer. Then, 0.2 mL of a 4×10^{-3} M PAN solution and 0.4 mL of P-DMOA extraction solvent were added and the mixture was vortexed for 10 seconds to obtain a homogeneous mixture. Next, 0.4 mL of a 10 M NaOH solution was added to form a turbid solution, which allowed for the extraction of the PAN-Cd(II) complex in the aqueous media into DMOA. The turbid solution was then centrifuged at 6000 rpm for 5 minutes to separate the phases. The upper phase, containing the extraction solution, was collected after removal of the lower phase with a micropipette. The extraction solution was made up to 0.5 mL with concentrated HNO_3 and analyzed using FAAS.

3. Results and Discussion

3.1 Optimization of Switchable solvent based extraction system variables

In this study, switchable solvent based microextraction with flame atomic absorption spectrometry was successfully developed for the determination of Cd (II) ions in water samples. In order to provide high extraction efficiency, important parameters such as pH, ligand and NaOH concentration, amount of extraction solution were investigated and optimized.

The formation and extraction of metal-chelate complexes are significantly influenced by the pH of the solution, which also affects the solubility and stability of these complexes. Literature studies utilizing PAN as a complexing agent have reported complex formation in a basic environment (Table 1), which contributes to high extraction efficiency. In order to determine the most appropriate pH for the developed method, pH values within the range of 6-10 were investigated. As demonstrated in Figure 1, the best extraction efficiency was obtained at pH 8.5, ensuring a high extraction yield. Therefore, this pH was utilized in subsequent studies.

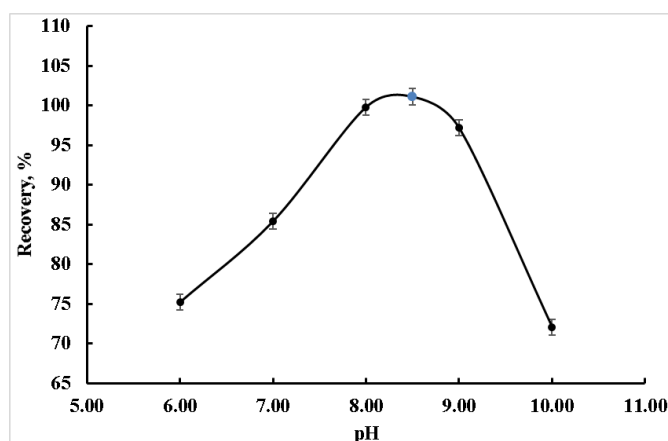


Fig.1. The effect of pH

PAN is a very good metal chelating agent that combines with Cd(II) in aqueous media. As shown in Table 1, PAN has been used for the determination of Cd(II) in many preconcentration methods.

Table 1. Different microextraction procedures using PAN as ligand for the determination of Cd (II) ions.

Method	pH	Reference
DLLME	9.0	4
FA-HLLME	8.5	22
RTIL– DLME	8.0	6
SS-LPME	7.5	7
USAE- SFODME	9.0	23

DLLME: Dispersive liquid–liquid microextraction

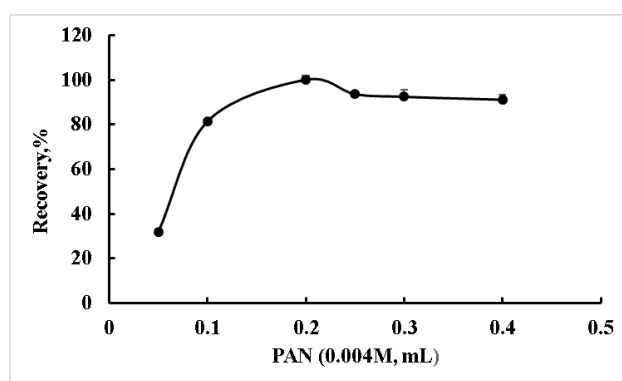
FA-HLLME: Flotation-Assisted homogenous liquid–liquid microextraction

RTIL: Room temperature ionic liquid

USAE: Ultrasound-assisted

PAN is a commonly employed chelating agent in the determination of diverse metal ions using colorimetric methods. It has low solubility in water and relatively high solubility in organic solvents. This property of PAN's low aqueous solubility enables its application in extractions that utilize appropriate organic solvents, making it a popular choice for separation, extraction, and detection of various metal ions. [24].

The most suitable amount of PAN that can be used to provide high extraction efficiency was investigated. For this purpose, the developed method was tested with different amounts of 5.10^{-3} M Ligand (0.05-0.4 mL). The optimum ligand amount was determined as 0.2 mL (Figure 2).

**Fig. 2.** The effect of PAN amount

The solvent pair DMOA / P-DMOA was used for the extraction of Cd(II) ions. The synthesized protonated N,N-dimethyl-n-octylamine (P-DMOA) has hydrophilic properties, while N,N-dimethyl-n-octylamine (DMOA) shows hydrophobic properties. Easily accessible, harmless and cheap CO₂ was used for conversion from DMOA structure to P-DMOA structure. In

addition, it was converted from the P-DMOA form to the DMOA form using NaOH, which is easily available in the laboratory environment.

The developed method to investigate the effect of extraction solvent volume on the extraction efficiency was carried out with different volumes of P-DMOA (0.2–0.7 mL). As shown in Figure 3, the absorbance signal increased to 0.4 mL as the amount of P-DMOA increased. After this amount, the extraction efficiency started to decrease. The most appropriate amount was found as 0.4 mL.

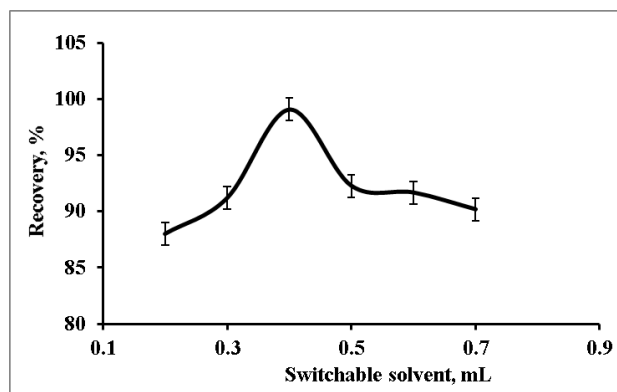


Fig. 3. The effect of P-DMOA amount

In order to obtain DMOA with nonpolar properties from P-DMOA with polar properties, it is necessary to remove CO₂ from the environment. There are several alternatives for this, such as adding NaOH and HCl to the solution, heating the solution, or passing N₂ gas through the solution. In this study, 10 M NaOH solution was used because it is fast and easy to use, creates the DMOA phase quickly, and is readily available and inexpensive.

The range of 0.1-0.6 mL was investigated to determine the optimum value of 10 M NaOH solution (Figure 4), and the optimal amount was found to be 0.4 mL. To create an apolar extraction solvent DMOA phase from polar P-DMOA, 0.4 mL of 10 M NaOH was added to all solutions.

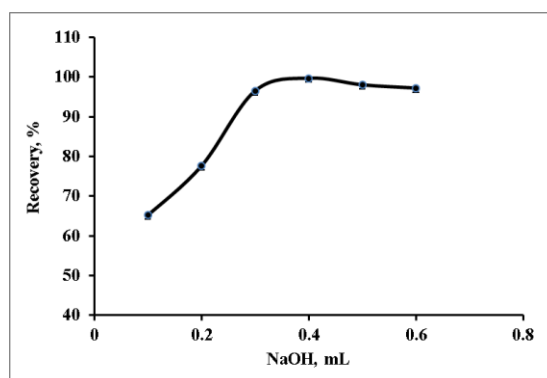


Fig. 4. The effect of NaOH (10M) amount

3.2 The effect of interference ions

While the analyte ion was determined by the developed microextraction method, the tolerance limits of various cation types that could cause interference were determined and their effects on

recovery were examined. As seen in Table 2, the studied foreign ions do not have a significant effect on their recovery to Cd (II) ions.

Table 2. Influences of selected interfere ions on the recoveries of Cd (II) (N=3).

Ion	Added as	Concentration Ratio (Interfere ion/Cd(II))	Recovery (%)
Fe (III)	Fe (NO ₃) ₃	30	97.5±1.1
Cr(III)	Cr(NO ₃) ₃	30	94.1±3.2
Pb (II)	Pb(NO ₃) ₂	20	94.7±1.3
Ni (II)	Ni(CH ₃ COO) ₂	20	98.5±1.6
Co (II)	CoCl ₂	20	96.3±1.4
Cu (II)	Cu(CH ₃ COO) ₂	20	97.7±0.8

3.3 The effect of sample volumes

In extraction studies of trace species from samples, the sample volume is crucial for achieving a higher enrichment factor. The various volumes of sample solutions were used containing the same amount of Cd(II) ions between 5-50 mL, while keeping other conditions fixed. The results of the study showed that the extraction method was able to give quantitative results up to 30 mL of sample volume. This suggests that the method may not be suitable for larger sample volumes, as the recovery of Cd(II) ions may be compromised beyond this point.

3.4 Analytical parameters

The analytical properties of the proposed SS-LPME method were evaluated under optimized conditions. The limit of detection (LOD) and limit of quantification (LOQ) were determined using the $3S_b/m$ and $10S_b/m$ formulas, respectively, where S_b is the standard deviation of the blank solution and m is the slope of the calibration equation. The LOD and LOQ for Cd(II) were found to be $0.63 \mu\text{g L}^{-1}$ and $2.1 \mu\text{g L}^{-1}$, respectively.

The preconcentration factor (P.F.) was calculated as the ratio of the highest sample volume (30 mL) to the lowest final volume (0.5), which resulted in a P.F. of 60. This indicates that the SS-LPME method is capable of enriching the concentration of Cd(II) in water samples by a factor of 60, which is a significant improvement over direct analysis.

The relative standard deviation (RSD) at a concentration level of $40 \mu\text{g L}^{-1}$ of Cd(II) was determined to be 2.8 % (N=5), which indicates good precision of the method. This low RSD value shows that the method is reproducible and reliable for the determination of Cd(II) in aqueous samples.

When some parameters of the developed method (RSD%, LOD, E.F/P.F) were compared with some previously reported methods, it was observed that the method has a good LOD and P.F.(Table 3)

In summary, the optimized SS-LPME method has a low LOD and LOQ, high preconcentration factor, and good precision, making it a suitable analytical technique for the determination of trace amounts of Cd(II) in water samples.

Table 3. Comparison of some new separation and preconcentration methods using FAAS and Cd(II) ion analysis.

Method/ Detection	E.F/P.F	LOD (μgL^{-1})	RSD%	Reference
DLLME	34.5	1.2	2.1	25
SPE	2.4	1.7	-	26
CPE	-	0,31	2.4	27
SS-LPME	60	0.63	2.8	This study

3.5 Application

The method was applied to environmental water samples, including tap water, river water, and rainwater, to determine the content of Cd(II). To prepare the samples, they were first filtered through a 0.45 μm mesh size membrane filter and then stored in polyethylene bottles at 4°C in the dark.

To check the accuracy of the method, different amounts of Cd(II) were added to the samples, and the recovery values were determined. The results showed that the recoveries of Cd(II) ions were in the range of 97.5% to 102%, indicating that the method is accurate in determining the Cd(II) content in environmental water samples.

Table 4 shows the different Cd(II) amounts added to the samples and the corresponding recovery values obtained from the analysis. The results showed that the method is reliable and can be used to accurately determine the Cd(II) content in environmental water samples.

Table 4. Determination of Cd(II) in tap. river water samples (N=3).

Sample	Added Cd(II) (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
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	0	-	-
Tap water	0.05	0.051±0.0003	102.0
	0.08	0.0804±0.0002	100.5
	0	-	-
River water	0.05	0.0495±0.002	99.0
	0.08	0.078±0.004	97.5
	0	-	-
Rain water	0.05	0.0508±0.001	101.6
	0.08	0.0794±0.003	99.25

4. Conclusion

A quick and effective preconcentration method for cadmium ion detection in water samples using SHS-LPME was successfully developed for FAAS determination. The results of the addition recovery tests demonstrated that the presented procedure is applicable for real samples, as indicated by the quantitative recoveries obtained (>99%). This method utilizes environmentally friendly solvents and offers benefits such as simplicity, speed, and affordability. Additionally, it achieves high accuracy in detecting low levels of cadmium ions in aqueous samples.

Ethics in Publishing

There are no ethical issues regarding the publication of this study

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